

Supporting Information

**Suppression of H<sub>2</sub> bubble formation on an electrified Pt electrode interface in an acidic “water-in-salt” electrolyte solution**

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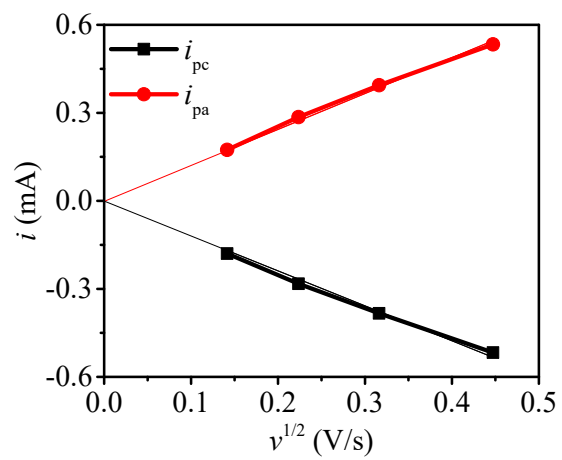
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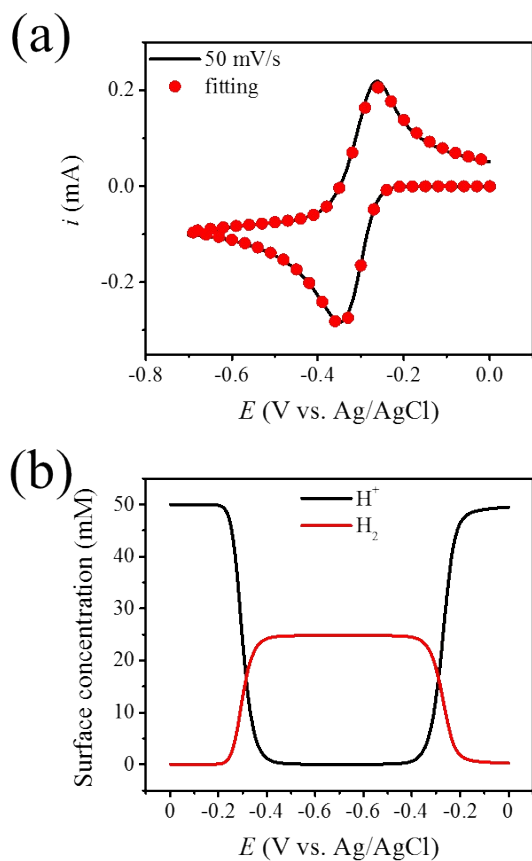
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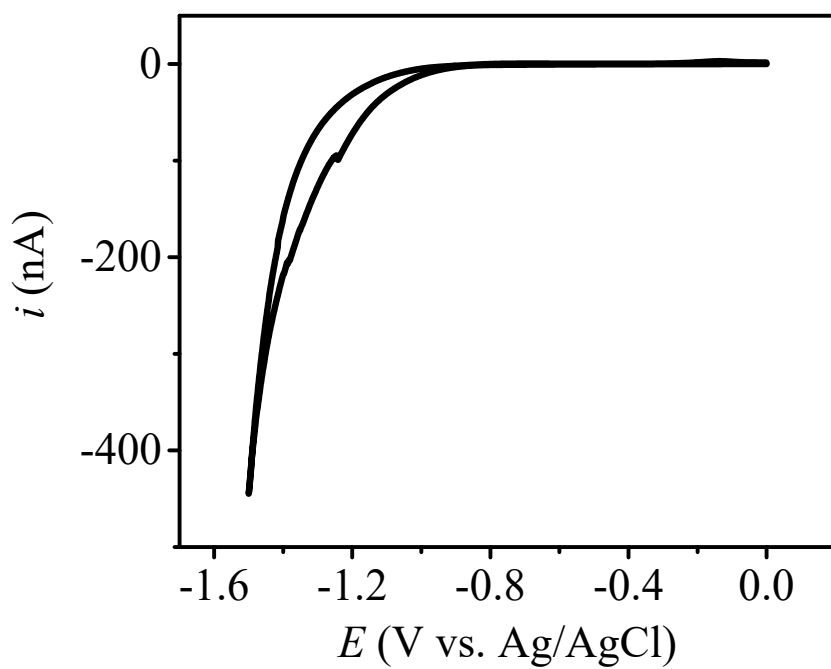
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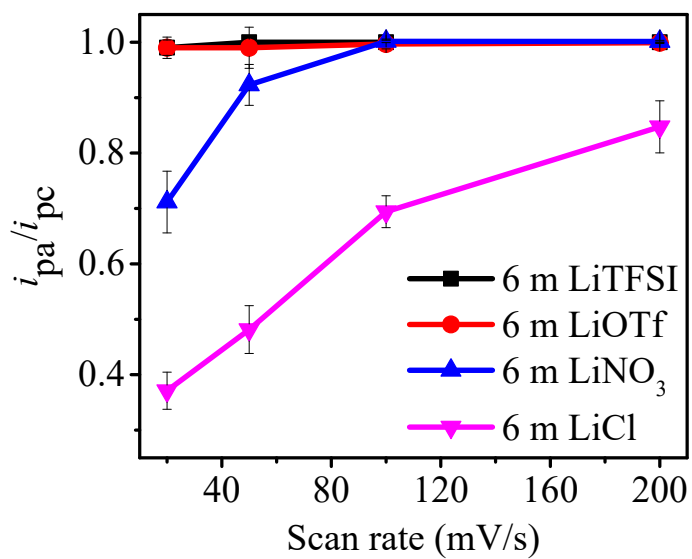
**Figure S1.** The linearity of  $i_{pc}$  and  $i_{pa}$  as a function of  $v^{1/2}$ .



**Figure S2.** (a) The CV at 50 mV/s on a Pt MDE in a 6 m LiTFSI solution containing 50 mM HClO<sub>4</sub> (black line) and the best-fit simulation result (red circle), and (b) the surface concentration profiles of chemical species from the simulated CV in a. For the simulation, the  $e^-$ -transfer rate constant,  $k^0$ , and the transfer coefficient,  $\alpha$ , were set to be 0.1 cm/s and 0.5, respectively.

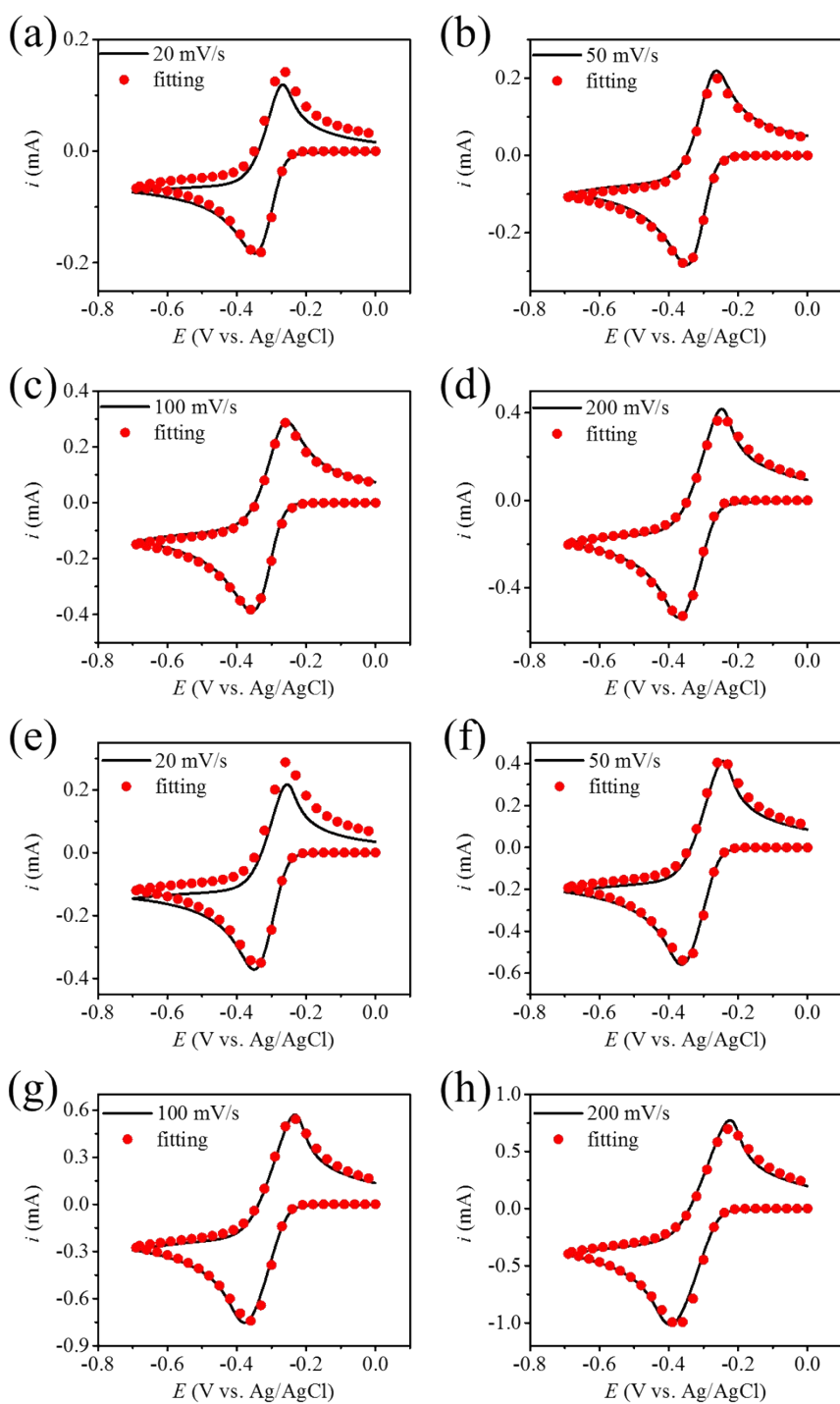


**Figure S3.** The CV in an aqueous 6 m LiTFSI solution without HClO<sub>4</sub> on a Pt UME at 20mV/s.

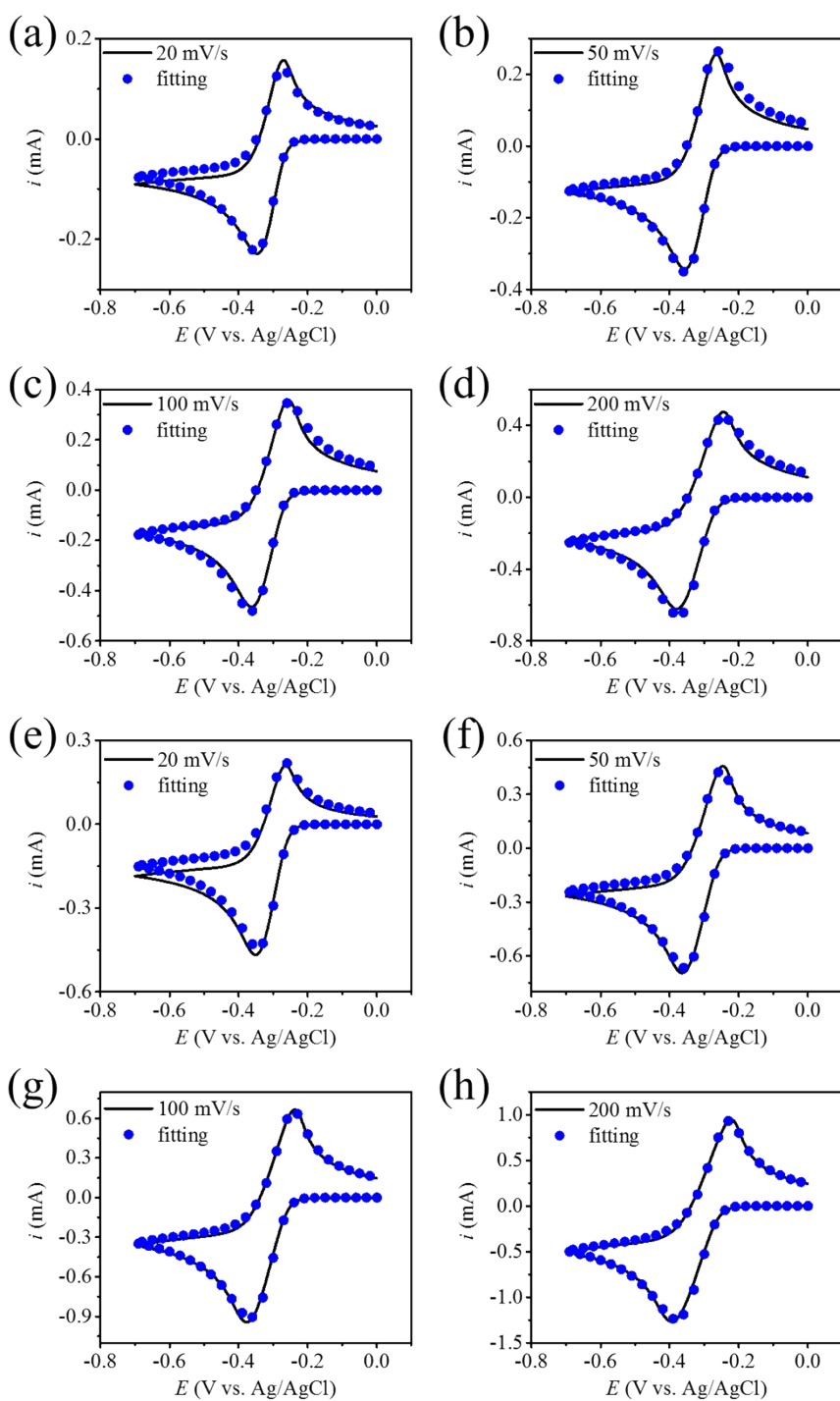


**Figure S4.** The  $i_{pa}/i_{pc}$  vs.  $\nu$  plots in aqueous solutions containing the four different types electrolytes with 25 mM HClO<sub>4</sub>.

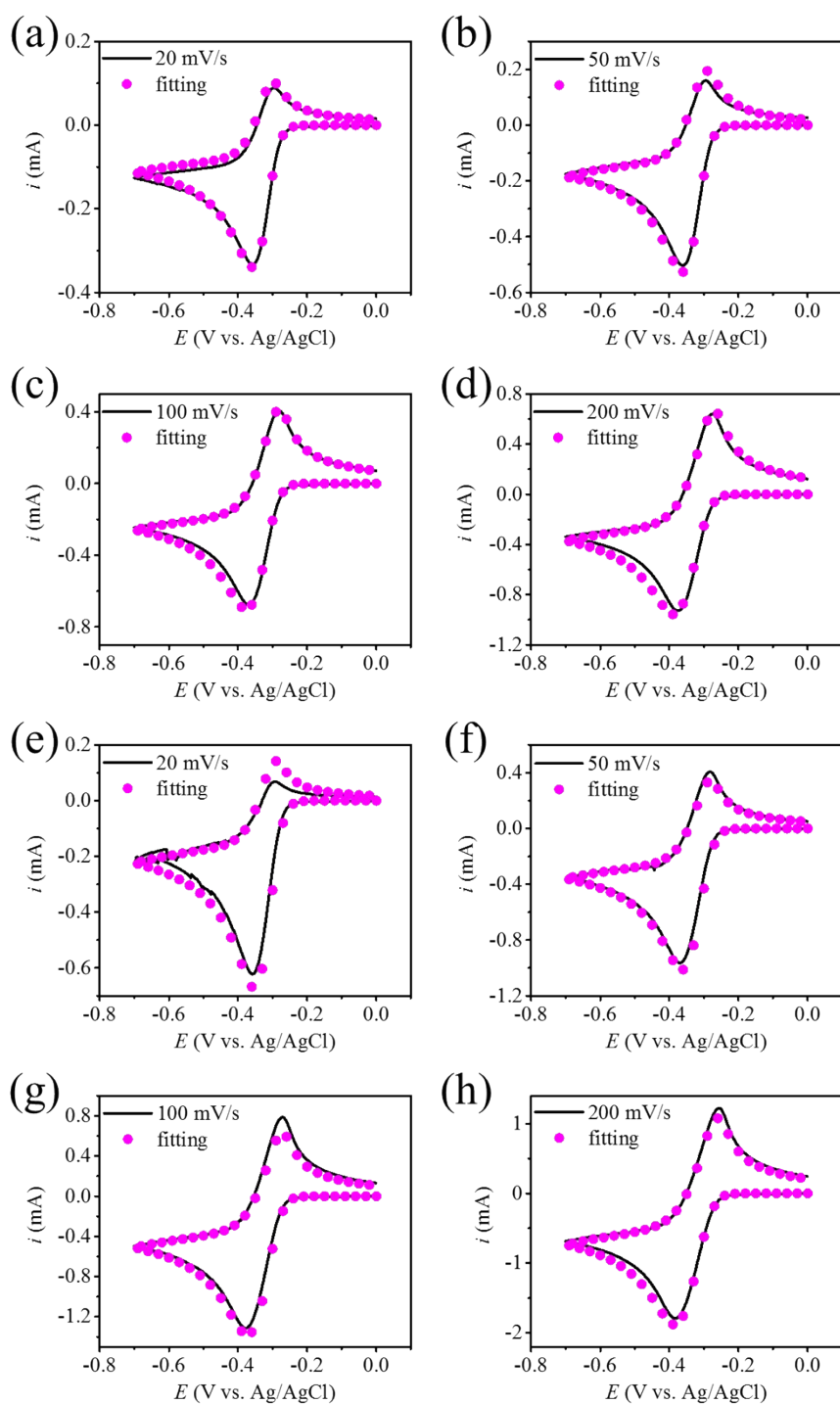




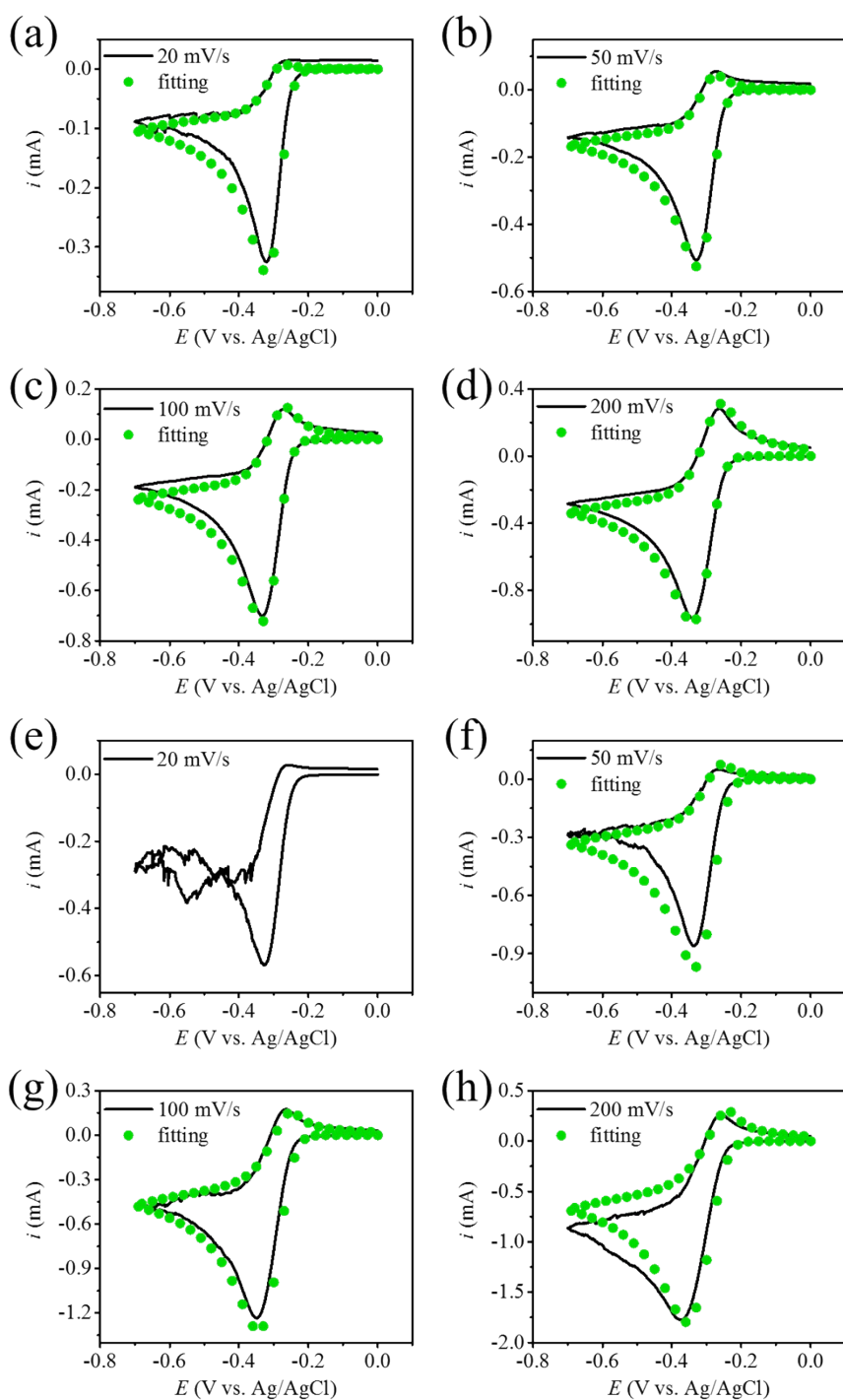
**Figure S5.** The CVs (black line) at various  $\nu$  (20, 50, 100, and 200 mV/s) on a Pt MDE in 6 m LiTFSI solutions containing either (a-d) 50 or (e-h) 100 mM  $\text{HClO}_4$ , and the corresponding best-fit simulation results (dotted red circle).



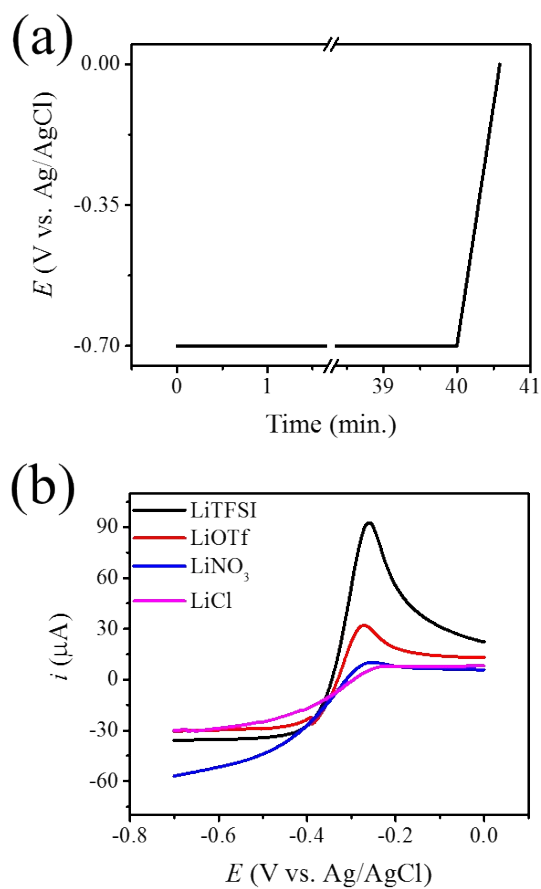
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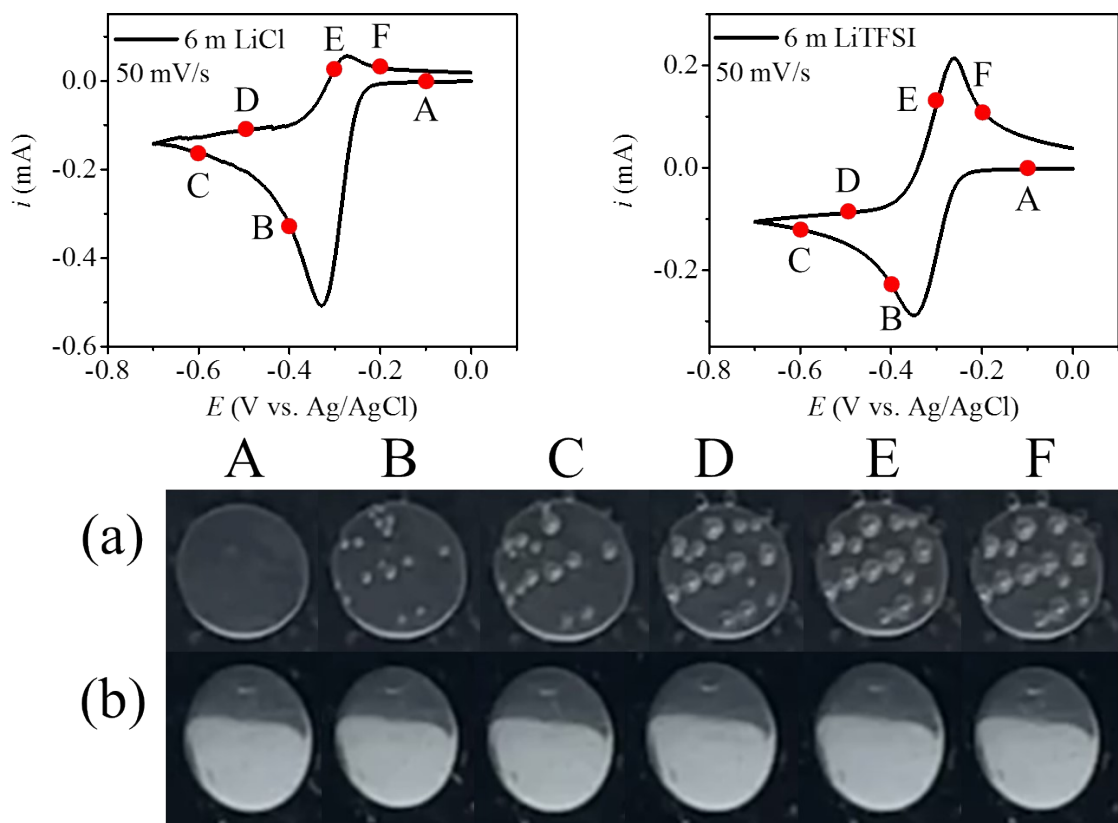
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**Figure S8.** The CVs (black line) at various  $v$  (20, 50, 100, and 200 mV/s) on a Pt MDE in 6 m LiCl solutions containing either (a-d) 50 or (e-h) 100 mM  $\text{HClO}_4$ , and the corresponding best-fit simulation results (dotted green circle). For the CV in e, the experimentally obtained CV was too distorted to be fitted by the digital simulation due to the adsorption of  $\text{H}_2$  bubbles on an electrode surface.



**Figure S9.** (a) The electrode potential profile vs.  $t$  for (b) the resulting voltammograms at 20 mV/s, which were measured from acidic solutions with the four different types of 6 m electrolytes.



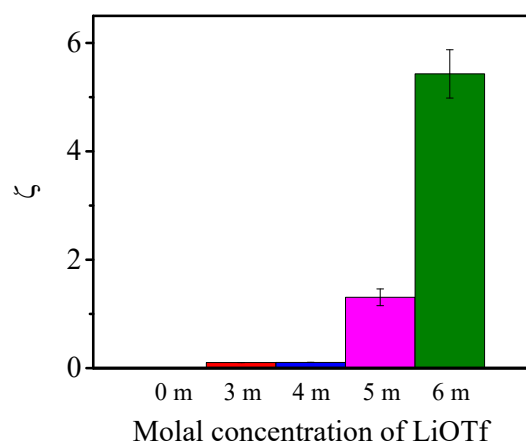
**Figure S10.** The sequential snapshots of H<sub>2</sub> bubble formation on a Pt MDE during cyclic voltammetry for H<sup>+</sup>/H<sub>2</sub> redox reaction in 50 mM HClO<sub>4</sub> solutions containing either (a) 6 m LiCl or (b) the same molal concentration of LiTFSI.

**Note S1. Estimation for thickness of a modulation layer**

The thickness of the modulation layer ( $\lambda$ ) in solutions with different types of 6 m electrolytes were estimated by the following equation.<sup>1</sup>

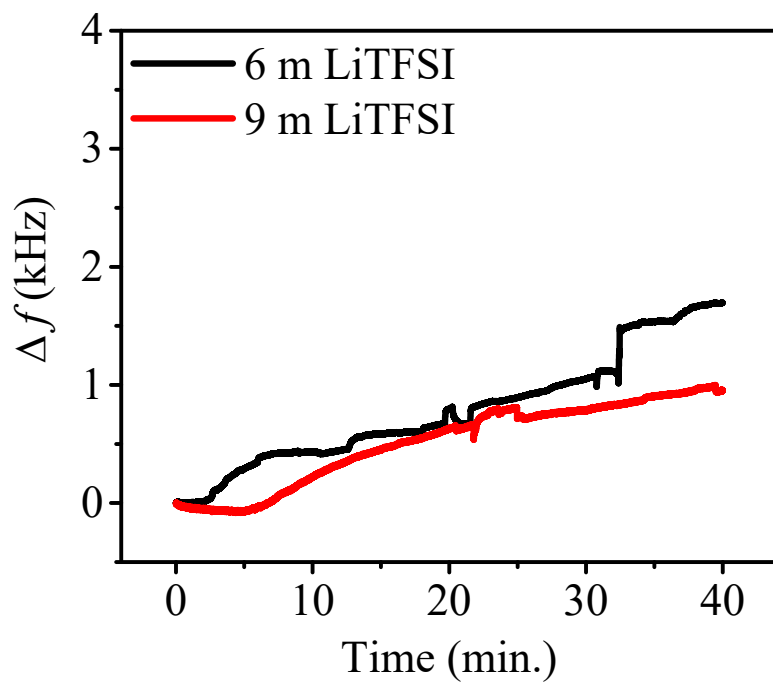
$$\lambda = \frac{1}{2} \left( \sqrt{\frac{\rho\omega}{2\eta}} \right)^{-1} \quad (1)$$

Here,  $\omega$  is the resonant frequency of the fundamental mode,  $\rho$  is the liquid density, and  $\eta$  is the liquid viscosity. Each of the corresponding parameters and the estimated  $\lambda$  in the different electrolytes solutions are listed in Table S2.



**Figure S11.** The  $\zeta$ -histograms obtained from  $\Delta f$  vs.  $t$  curves in acidic solutions containing various molal concentrations of LiOTf.

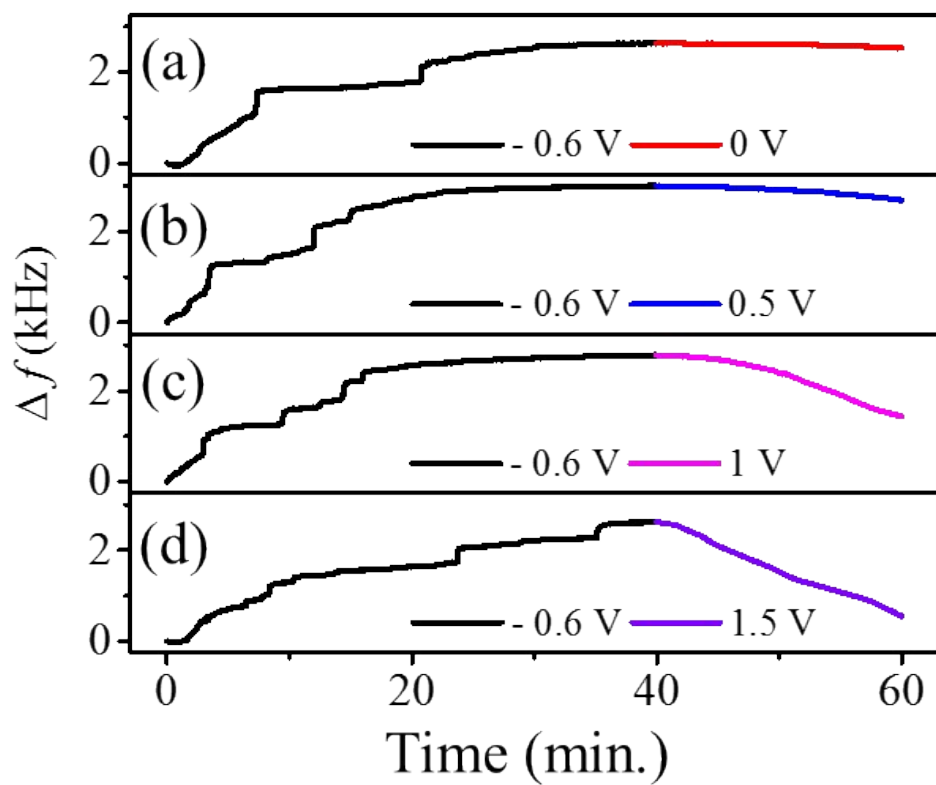




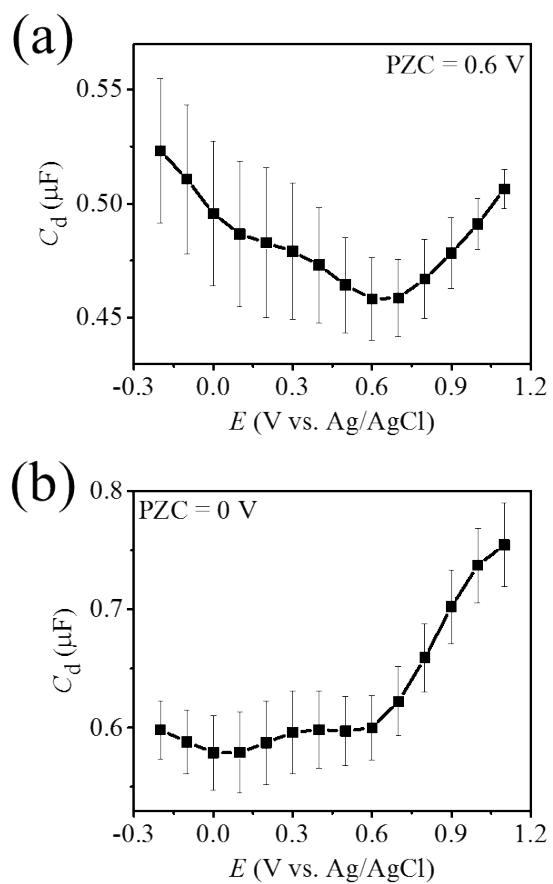
**Figure S12.** The  $\Delta f$  vs.  $t$  curves during HER on Pt electrodes in 50 mM HClO<sub>4</sub> solutions containing 6 m LiTFSI (black) and 9 m LiTFSI (red) through the EQCM measurements.

**Note S2. The EQCM measurements for retention of electrogenerated H<sub>2</sub> bubbles on a Pt electrode as a function of applied potentials**

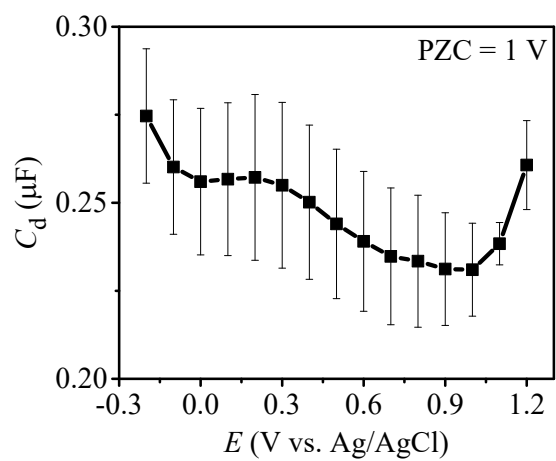
We chose an aqueous acidic solution containing 3 m LiTFSI as a model electrolyte condition. For the EQCM measurements, -0.6 V was constantly applied for 40 minutes to drive HER, and the potential was stepped to various positive values for another 20 minutes. After  $\Delta f$  increased and reached at the equilibrium under at constantly applied -0.6 V for 40 min., the potential was stepped to either 0 or 0.5 V, and  $\Delta f$  barely decreased (see Figure S9a-b). As the electrode potential was positively stepped to 1 and 1.5 V (Figure S9c-d),  $\Delta f$  instantaneously reduced, and in the case of 1.5 V,  $\Delta f$  was even reduced to  $\sim 0$ .



**Figure S13.** The  $\Delta f$  vs.  $t$  curves measured in acidic 3 m LiTFSI solutions on a Pt electrode as the electrode potential was applied to -0.6 V for 40 minutes and stepped to (a) 0, (b) 0.5, (c) 1, and (d) 1.5 V vs. Ag/AgCl, respectively.



**Figure S14.** The  $C_d$  as a function of the electrode potentials (vs. Ag/AgCl) on Pt MDEs in 6 m (a) LiTFSI and (b) LiOTf solutions.



**Figure S15.** The  $C_d$  as a function of the electrode potentials (vs. Ag/AgCl) on an Au MDE in a 6 m LiTFSI solution.

**Table S1.** The reaction parameters for the simulation results in Figure S5-S8. The transfer coefficients of all the charge transfer reactions were assumed to be 0.5.

	6 m LiTFSI	6 m LiOTf	6 m LiNO <sub>3</sub>	6 m LiCl
Diffusion coefficient	$D_{H^+} = 9 \times 10^{-6} \text{ cm}^2/\text{s}$	$D_{H^+} = 1.4 \times 10^{-5} \text{ cm}^2/\text{s}$	$D_{H^+} = 3 \times 10^{-5} \text{ cm}^2/\text{s}$	$D_{H^+} = 3 \times 10^{-5} \text{ cm}^2/\text{s}$
Charge transfer reaction $H^+ + e^- \rightleftharpoons H$	$E^0 = -0.4 \text{ V}$ $k_{ct} = 0.03 \text{ cm/s}$	$E^0 = -0.4 \text{ V}$ $k_{ct} = 0.03 \text{ cm/s}$	$E^0 = -0.4 \text{ V}$ $k_{ct} = 0.03 \text{ cm/s}$	$E^0 = -0.4 \text{ V}$ $k_{ct} = 0.03 \text{ cm/s}$
Chemical reaction $H + H \rightleftharpoons H_2$	$K_{eq} = 2 \times 10^4 \text{ M}^{-1}$ $k_f = 2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	$K_{eq} = 2 \times 10^4 \text{ M}^{-1}$ $k_f = 2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	$K_{eq} = 2 \times 10^4 \text{ M}^{-1}$ $k_f = 2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	$K_{eq} = 2 \times 10^4 \text{ M}^{-1}$ $k_f = 2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$
$H_2 + H_2 \rightleftharpoons (H_2)_2$	$K_{eq} = 3.5 \times 10^8 \text{ M}^{-1}$ $k_f = 0.01 \text{ M}^{-1}\text{s}^{-1}$	$K_{eq} = 3.5 \times 10^8 \text{ M}^{-1}$ $k_f = 0.6 \text{ M}^{-1}\text{s}^{-1}$	$K_{eq} = 3.5 \times 10^8 \text{ M}^{-1}$ $k_f = 4 \text{ M}^{-1}\text{s}^{-1}$	$K_{eq} = 3.5 \times 10^8 \text{ M}^{-1}$ $k_f = 56 \text{ M}^{-1}\text{s}^{-1}$

**Table S2.** The measured parameters in acidic solutions containing different types of 6 m electrolytes for the calculation of the thickness of the modulation layers,  $\lambda$ .

	<b>No Li electrolytes</b>	<b>6 m LiTFSI</b>	<b>6 m LiOTf</b>	<b>6 m LiNO<sub>3</sub></b>	<b>6 m LiCl</b>
$\eta$ (cp)	0.91	4.51	3.4	2.2	1.9
$\rho$ (g/cm <sup>3</sup> )	1.03	1.44	1.33	1.2	1.12
$\lambda$ (nm)	220	420	380	320	308

## References

1. S. Na Songkhla and T. Nakamoto, *Chemosensors*, 2021, **9**, 350.